THEORETICAL INVESTIGATION OF THE UV-VIS PHOTODISSOCIATION DYNAMICS OF $Ar_n(BRCN^-)$

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We present the results of quantum dynamics studies of photodissociation of $BrCN^-$ following electronic excitation to states that dissociate to Br^- + CN and Br* + CN^-. The electronic structure of $BrCN^-$ was evaluated with MRCI-SO/aug-cc-pVTZ at a fixed CN distance of 1.18 $\AA$. The calculations were used to evaluate the two-dimensional potential surfaces for the ground and excited states as functions of the Br-CN(center of mass) distances, R, and angles, θ, between CN and R. A diabatic model developed for the two relevant excited states shows a dramatic change in the electronic character of the states near the $BrCN^-$ geometry when $\theta \leq \pi/2$. The quantum dynamics studies on the bare $BrCN^-$ were carried out by exciting wave packets of six vibrational states of $BrCN^-$ that are thermally populated at 150K onto each of the two excited states. Upon excitations of the wave packets onto the state accessible in the visible region, 51% Br^- and 49% CN^- photoproducts were calculated. Similar calculations in the UV region yielded 56% Br^- and 44% CN^- photoproducts. Experimentally, when $BrCN^-$ is excited in the visible region, 60% Br^- and 40% CN^- photoproducts are obtained while 80% Br^- and 20% CN^- yields were obtained in the UV region. Further dynamics studies of $BrCN^-$ solvated in argon will be carried out with varying $Ar_n(BrCN^-)$ cluster sizes.